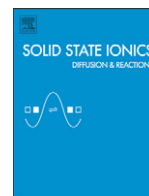




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The correlation between surface kinetic and bulk diffusion properties of proton conducting oxides

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ABSTRACT

The correlation between surface kinetic and diffusion properties of proton conducting oxides is addressed in this work. Thermogravimetric relaxation measurements have been undertaken for three different oxides, and the same correlation between surface exchange coefficients (k) and bulk diffusion coefficients (D) is found to hold for both hydrogen tracer transport and chemical transport of water across several orders of magnitude. On account of the prevailing kinetic regimes we argue that the observed k - D correlations must be ascribed the materials transport properties rather than an inherent parameter interrelation. It is conceivable that the same elementary step in the reaction scheme for dissolution of water is rate limiting for all the data sets approximating the same linear power law. The only data sets significantly departing from this trend are recorded under conditions where the surface exchange appears to be dominated by a reaction with molecular hydrogen. When evaluating surface exchange coefficients it may also be necessary to take the resistivity stemming from separation of charge carriers in subsurface space charge regions into account.

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1. Introduction

The ratio between bulk transport and surface exchange rates of mixed proton-electron conducting oxides comprises a parameter predicting within which kinetic regime a hydrogen separation membrane with defined thickness operates. The surface exchange reaction on proton conducting oxides is not well understood, – neither particularly explored – but because thin film processing is turning ever more sophisticated, surface limited transport rates are becoming an increasingly relevant issue to address. Protons enter these oxides primarily via hydration of oxygen vacancies according to



The overall reaction driving H_2 separation through dense oxides at steady state conditions is on the other hand oxidation of hydrogen forming protons and electrons: $\text{H}_2(\text{g}) + 2\text{O}_\text{O}^{\text{x}} = 2\text{OH}_\text{O}^{\bullet} + 2\text{e}^-$. It is therefore of outmost relevance to scrutinize the interaction of these oxide surfaces with both H_2O and H_2 .

The correlation between surface exchange and bulk diffusion can also hold important information about the fundamental, functional relation between these processes and thereby illuminate the mechanistic properties of the otherwise veiled surface exchange reaction. In the case of oxide ion conductors, a general correlation between the kinetic and diffusion properties was disclosed years back by Kilner and De

Souza [1,2], showing that when the logarithm of the ^{18}O tracer surface exchange coefficients (k_O^δ) are plotted against the logarithm of the corresponding tracer diffusion coefficients (D_O^δ), the experimental data points approximates a linear power law. The data points furthermore tend to cluster into two groups depending only on whether electronic or ionic conductivity is dominant in the materials. This rather famous plot is reproduced in Fig. 1. Here the oxides sorting into the group with the smallest slope (between 1/2 and 1) are all electron-rich perovskites, whereas the materials in the group with “slow” surfaces (having slopes of 3–4) are generally electron-poor and primarily considered as electrolyte candidates. The fact that the k - D correlations of oxygen tracer data have such a systematic character and cover a range of up to ten orders of magnitudes have led to the widespread assumption that there is a fundamental link between surface and bulk properties within families of materials.

The mapping of surface exchange rates and its relation to bulk diffusion is, based on the above accounts, of both technological relevance and fundamental interest. The main purpose of this work is to compile the phenomenological transport coefficients of proton conducting oxides in a similar fashion to the plot in Fig. 1. Both the tracer surface exchange and diffusion coefficients (for brevity denoted k^* and D^* herein) and the chemical surface exchange and diffusion coefficients k^δ and D^δ are included in the assessment of correlated transport rates. The transport parameters have been collected from transient thermogravimetric (TG) measurements on three renowned oxides in the field of high-temperature proton conductivity: $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCY), $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZY) and $\text{La}_{27.15}\text{W}_{4.85}\text{O}_{55.28}\text{V}_{0.73}$ (LWO). As one of few studies concurrently assigning both surface kinetic and bulk diffusion properties to this class

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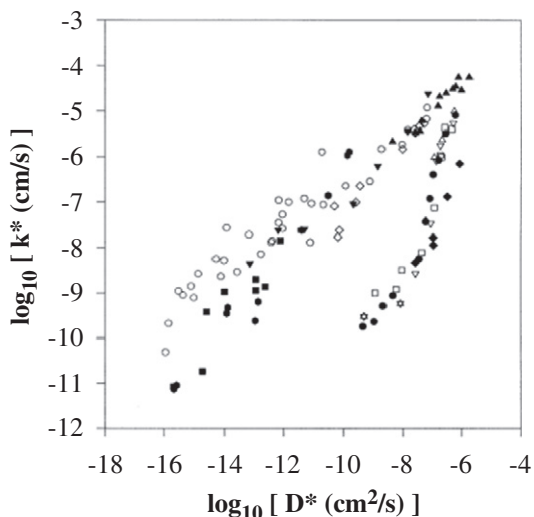


Fig. 1. Correlation of the ^{18}O tracer surface exchange coefficients with the tracer diffusion coefficient (taken from ref. [1] with permission from Elsevier). The data points clustering in the group with the smaller slope of approximately 1/2 are recorded for electron rich transition metal oxides, and the other data points are recorded for electron-poor materials. The reader is referred to the original publication for decipherment of the various oxide compositions.

of oxides based on a single experimental technique, we are in a unique position to collate and compare the data sets.

2. Experimental

The preparation of slab samples of LWO and BCY has been reported in an earlier publication [3]. BZY powder was manufactured by spray pyrolysis (CerPoTech, Norway). The powder was isostatically pressed into disk shaped samples with green body diameters of 13 mm and sintered in air at 1650 °C for 3 h and at 1600 °C for 7 h, yielding disks with a relative density of 94%. Generally two slabs of different thicknesses (operating in different kinetic regimes) were employed for each compound with the purpose of reliably determine both surface kinetic and bulk diffusion properties at – to the extent possible – each temperature.

Hydrogen tracer transients (denoted *) were induced by exchanging between H_2O and D_2O wetted gases at chemical equilibrium, whereas

chemical transients (denoted δ) were recorded in response to small perturbations in the water vapor pressure (controlled by mixing gases passed through saturated KBr (aq) and P_2O_5 (s) in the appropriate ratios). Chemical and tracer relaxation measurements were conducted in both wetted synthetic air ($p_{\text{O}_2} = 0.21$ atm) and in 5% H_2 or D_2 /balance Ar ($p_{\text{O}_2} \approx 10^{-11}$ – 10^{-20} atm). Complete experimental details and the mathematical solution used to curve fit the mass relaxations are reported in earlier publications [3,4].

3. Results and discussion

3.1. Temperature- and p_{O_2} -dependencies of transport coefficients

Fig. 2a–c depicts the various phenomenological surface exchange coefficients and bulk diffusion coefficients of LWO, BZY and BCY as a function of reciprocal temperature in wetted air (oxidizing) and in wetted 5% H_2 (reducing). The respective activation energies are included in Table 1. The chemical coefficients D^δ and k^δ are depicted at the higher temperatures because hydration is sluggish and could only be measured between, typically, 500 and 800 °C. Tracer relaxation measurements are restricted to lower temperatures where (i) the concentration of protons is sufficiently large to give a measurable weight change and (ii) the materials are fully hydrated and thus not inflicted by the differences in vapor pressure of H_2O and D_2O [5].

The tracer relaxation measurements under reducing conditions ($\text{H}_2/\text{H}_2\text{O}-\text{D}_2/\text{D}_2\text{O}$) were only carried out for the thinnest specimens of LWO and BCY (0.05 cm) which didn't provide any information about the hydrogen tracer diffusion coefficients D^* . In the case of BZY (Fig. 2b), D^* was inaccessible even from the relaxation curves of the thickest sample of 0.1 cm. It should also be noted that the chemical surface exchange coefficients (k^δ) of LWO and BZY have a pronounced oxygen partial pressure dependency in which the activation energies under reducing conditions are significantly smaller than under oxidizing.

The chemical diffusion coefficients D^δ do not reveal any oxygen partial pressure dependencies even though it is well-documented that the hydration mechanism of inter alia BZY and BCY is highly p_{O_2} -dependent [6,7]. Proton conducting oxides namely hydrate by a two-fold mechanism when the concentration of electronic charge carriers is sufficiently large (at high p_{O_2} s in the case of p-type conducting BZY and BCY). This mechanism is typically manifested in non-monotonic conductivity relaxation curves and occurs because the reaction depicted in Eq. (1) decomposes into two redox reactions [7–9]. LWO relaxes by comparison monotonically under oxidizing conditions (negligible p-type conductivity) [10], but

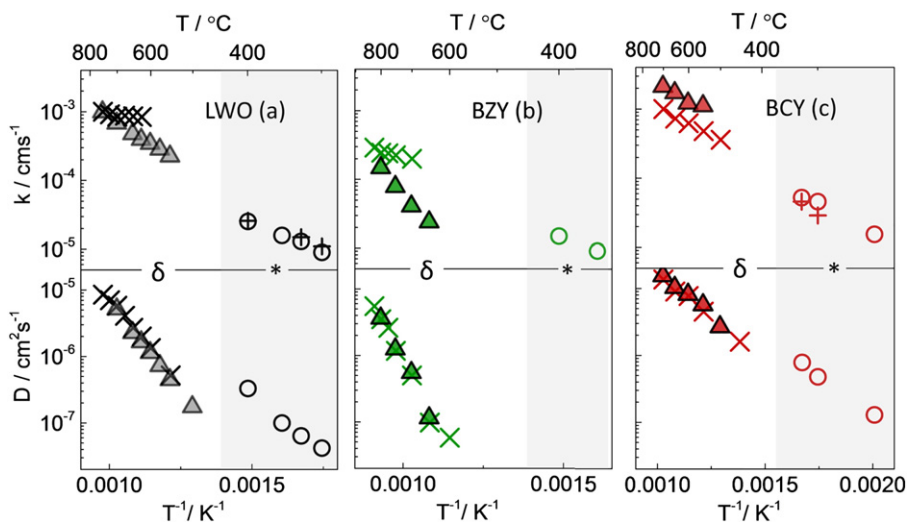


Fig. 2. Surface exchange coefficients k and diffusion coefficients D of LWO (a), BZY (b) and BCY (c). Oxidizing and reducing conditions are for chemical transport coefficients (δ) labelled Δ and \times , and for tracer coefficients \circ and $+$ (plotted in the shaded areas).

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